

## PCT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

DE BRUIJN, Leendert, C.  
Nederlandsch Octrooibureau  
Scheveningseweg 82  
P.O. Box 29720  
NL-2502 LS The Hague  
PAYS-BAS

Date of mailing (day/month/year) 19 July 2001 (19.07.01)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference BO 42044	
International application No. PCT/NL99/00814	International filing date (day/month/year) 29 December 1999 (29.12.99)

1. The following indications appeared on record concerning:		
<input checked="" type="checkbox"/> the applicant	<input checked="" type="checkbox"/> the inventor	<input type="checkbox"/> the agent <input type="checkbox"/> the common representative
Name and Address GOTTLIEB, Kornelis, Fester Wildervankstraat 12 NL-9643 LC Wildervank Netherlands	State of Nationality NL	State of Residence NL
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:		
<input type="checkbox"/> the person	<input type="checkbox"/> the name	<input checked="" type="checkbox"/> the address <input type="checkbox"/> the nationality <input type="checkbox"/> the residence
Name and Address GOTTLIEB, Kornelis, Fester Stoepveldsingel 119 NL-9403 SM Assen Netherlands	State of Nationality NL	State of Residence NL
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
3. Further observations, if necessary:		
4. A copy of this notification has been sent to:		
<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned	
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned	
<input type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:	

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer S. Buttay
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

## PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

To:

DE BRUIJN, Leendert, C.  
Nederlandsch Octrooibureau  
Scheveningseweg 82  
P.O. Box 29720  
NL-2502 LS The Hague  
PAYS-BASDate of mailing (day/month/year)  
21 June 2001 (21.06.01)Applicant's or agent's file reference  
BO 42044International application No.  
PCT/NL99/00814

## IMPORTANT NOTIFICATION

International filing date (day/month/year)  
29 December 1999 (29.12.99)

## 1. The following indications appeared on record concerning:

☒ the applicant ☒ the inventor ☐ the agent ☐ the common representative

## Name and Address

STAPPERS, Frank, H., M.  
Broekeindweg 10  
NL-571 NZ Grubbenvorst  
Netherlands

## State of Nationality

NL

## State of Residence

NL

Telephone No.

Facsimile No.

Teleprinter No.

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☐ the name ☒ the address ☐ the nationality ☐ the residence

## Name and Address

STAPPERS, Frank, H., M.  
Broekeindweg 10  
NL-5971 NZ Grubbenvorst  
Netherlands

## State of Nationality

NL

## State of Residence

NL

Telephone No.

Facsimile No.

Teleprinter No.

## 3. Further observations, if necessary:

## 4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned  
☐ the International Searching Authority ☒ the elected Offices concerned  
☐ the International Preliminary Examining Authority ☐ other:The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Authorized officer

S. Buttay

Facsimile No.: (41-22) 740.14.35

Telephone No.: (41-22) 338.83.38

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
 United States Patent and Trademark  
 Office  
 Box PCT  
 Washington, D.C.20231  
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

<b>Date of mailing (day/month/year)</b> 28 August 2000 (28.08.00)	
<b>International application No.</b> PCT/NL99/00814	<b>Applicant's or agent's file reference</b> BO 42044
<b>International filing date (day/month/year)</b> 29 December 1999 (29.12.99)	<b>Priority date (day/month/year)</b> 30 December 1998 (30.12.98)
<b>Applicant</b> VAN SOEST, Jeroen, Johannes, Gerardus et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

25 July 2000 (25.07.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was  
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland  Facsimile No.: (41-22) 740.14.35	<b>Authorized officer</b>  Juan Cruz  Telephone No.: (41-22) 338.83.38
--	--

PCT

NOTICE INFORMING THE APPLICANT OF THE  
COMMUNICATION OF THE INTERNATIONAL  
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

DE BRUIJN, Leendert, C.  
Nederlandsch Octrooibureau  
Scheveningseweg 82  
P.O. Box 29720  
NL-2502 LS The Hague  
PAYS-BAS

INGEA 24 JUL 2000

Date of mailing (day/month/year) 13 July 2000 (13.07.00)		
Applicant's or agent's file reference BO 42044		
International application No. PCT/NL99/00814	International filing date (day/month/year) 29 December 1999 (29.12.99)	Priority date (day/month/year) 30 December 1998 (30.12.98)
Applicant INSTITUUT VOOR AGROTECHNOLOGISCH ONDERZOEK (ATO-DLO) et al		

Pays-Bas  
IMPORTANT NOTICE

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:  
AU,CN,JP,KP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:  
AE,AL,AM,AP,AT,AZ,BA,BB,BG,BR,BY,CA,CH,CR,CU,CZ,DE,DK,DM,EA,EE,EP,ES,FI,GB,GD,GE,  
GH,GM,HR,HU,ID,IL,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MN,MW,MX,NO,NZ,  
OA,PL,PT,RO,RU,SD,SE,SG,SI,SK,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW  
The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on  
13 July 2000 (13.07.00) under No. WO 00/40617

**REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)**

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a **demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

**REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))**

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

## PATENT COOPERATION TREATY

09/869706

28 FEB 2000

PCT

From the INTERNATIONAL BUREAU

To:

DE BRUIJN, Leendert, C.  
Nederlandsch Octrooibureau  
Scheveningseweg 82  
P.O. Box 29720  
NL-2502 LS The Hague  
PAYS-BAS

**NOTIFICATION CONCERNING  
SUBMISSION OR TRANSMITTAL  
OF PRIORITY DOCUMENT**

(PCT Administrative Instructions, Section 411)

Date of mailing (day/month/year) 18 February 2000 (18.02.00)	
Applicant's or agent's file reference BO 42044	<b>IMPORTANT NOTIFICATION</b>
International application No. PCT/NL99/00814	International filing date (day/month/year) 29 December 1999 (29.12.99)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 30 December 1998 (30.12.98)
Applicant INSTITUUT VOOR AGROTECHNOLOGISCH ONDERZOEK (ATO-DLO) et al	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An asterisk(\*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
30 Dec 1998 (30.12.98)	1010926	NL	09 Febr 2000 (09.02.00)

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

Marc Salzman

Telephone No. (41-22) 338.83.38




# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference BO 42044		<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NL99/00814	International filing date (day/month/year) 29/12/1999	Priority date (day/month/year) 30/12/1998	
International Patent Classification (IPC) or national classification and IPC C08B31/00			
Applicant INSTITUUT VOOR AGROTECHNOLOGISCH ONDERZOEK et al			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 2 sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I <input checked="" type="checkbox"/> Basis of the report</li> <li>II <input type="checkbox"/> Priority</li> <li>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV <input type="checkbox"/> Lack of unity of invention</li> <li>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI <input checked="" type="checkbox"/> Certain documents cited</li> <li>VII <input checked="" type="checkbox"/> Certain defects in the international application</li> <li>VIII <input checked="" type="checkbox"/> Certain observations on the international application</li> </ul>			
Date of submission of the demand  25/07/2000		Date of completion of this report  13.02.2001	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer  Kairi, M  Telephone No. +49 89 2399 8672	



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/NL99/00814

**I. Basis of the report**

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

**Description, pages:**

1-11 as originally filed

**Claims, No.:**

1-14 as received on 22/01/2001 with letter of 22/01/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

**Re Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**Article 33(2) PCT**

None of the prior art discloses step b) of Claim 1 or that the second phase is a water-miscible nonsolvent for starch according to Claim 9.

**Article 33(3) PCT**

Closest prior art is considered to be the document DE-A-14 43 359 (D1) which discloses a process to directly obtain crosslinked starch in the form of granulates without requiring pulverization. D1 discloses in Example 1 that 100 g of starch which had been washed with water are dissolved in 280 ccm of water and 240 ccm of an aqueous 5 n solution of sodium hydroxide. The obtained solution is dispersed in a solution of 15 g cellulose acetate butyrate in 500 ccm ethylene dichloride. The dispersion is agitated for one hour in order to stabilize the drops of the starch solution in the dispersing medium. Subsequently 70 g 1,3-dichloropropanol are added. The reaction is performed at 50°C for 10 hours. After work up of the reaction mixture 93 g of a cross-linked product in the form of gel grains are obtained.

The subject-matter of Claim 1 differs from the disclosure in D1 in the step b which discloses i) dispersion or emulsifying of the second hydrophobic phase in the first phase, such that an oil-in-water emulsion is obtained; and ii) inversion of the oil-in-water emulsion to a water-in-oil emulsion.

The subject-matter of Claim 9 differs from D1 in that the second phase is a water-miscible non-solvent for starch.

The object of the present invention is to provide a method for the preparation of starch particles by means of which small starch particles having a particle size of 50 nm to a few mm can be obtained in a simple manner and can be used in pharmacy, cosmetics, foods, paints, coatings, paper, inks and many other applications.

The solution provided is non-obvious, since steps b) i) and ii) of Claim 1 and the feature that the second phase is a water-miscible non-solvent for starch according to Claim 9 are not disclosed in D1 or any other prior art and are not considered to be obvious.



## PATENT COOPERATION TREATY

PCT

09/869706

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>BO 42044</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/NL 99/ 00814</b>	International filing date (day/month/year) <b>29/12/1999</b>	(Earliest) Priority Date (day/month/year) <b>30/12/1998</b>
Applicant <b>INSTITUUT VOOR AGROTECHNOLOGISCH ONDERZOEK et al</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

## 4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

## 5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

## 6. The figure of the drawings to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

# INTERNATIONAL SEARCH REPORT

Int. Appl. No.

PCT/NL 99/00814

#6 09/8/99, 709

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08B31/00 C08J3/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 14 43 359 A (AKTIEBOLAGET PHARMACIA) 14 November 1968 (1968-11-14) page 4, last paragraph -page 6, paragraph 2; example 12	1-15
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 3 (C-203), 7 January 1984 (1984-01-07) & JP 58 171404 A (KOGYO GIJUTSUIN), 8 October 1983 (1983-10-08) abstract & DATABASE WPI Week 198346 Derwent Publications Ltd., London, GB; AN 817674 abstract	

-/-

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

24 March 2000

Date of mailing of the international search report

31/03/2000

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Lensen, H

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 99/00814

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	NL 7 402 700 A (A.E.STALEY MANUFACTURING COMPANY) 3 September 1974 (1974-09-03)	
P,X	WO 99 01214 A (ATO-DLO) 14 January 1999 (1999-01-14) see the whole document	1-15
P,X	EP 0 900 807 A (INSTITUUT VOOR AGROTECHNOLOGISCH ONDERZOEK) 10 March 1999 (1999-03-10) page 2, column 2, line 42 - line 52	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 99/00814

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 1443359	A	14-11-1968	SE 358894 B	13-08-1973
			GB 974054 A	
			NO 116690 B	05-05-1969
			US 3208994 A	28-09-1965
JP 58171404	A	08-10-1983	JP 1287106 C	31-10-1985
			JP 60011961 B	29-03-1985
NL 7402700	A	03-09-1974	AU 476973 B	07-10-1976
			AU 6490174 A	31-07-1975
			BE 810281 A	29-07-1974
			CA 1008069 A	05-04-1977
			DE 2408008 A	05-09-1974
			FI 59106 B	27-02-1981
			FR 2219974 A	27-09-1974
			GB 1418612 A	24-12-1975
			IT 1008975 B	30-11-1976
			JP 1132011 C	27-01-1983
			JP 49118783 A	13-11-1974
			JP 54003705 B	26-02-1979
			SE 416401 B	22-12-1980
			US 3876629 A	08-04-1975
WO 9901214	A	14-01-1999	NL 1006444 C	05-01-1999
			AU 8134198 A	25-01-1999
EP 900807	A	10-03-1999	AU 9008098 A	29-03-1999
			WO 9912976 A	18-03-1999



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C08B 31/00, C08J 3/16</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/40617</b> <b>(43) International Publication Date:</b> <b>13 July 2000 (13.07.00)</b>
<b>(21) International Application Number:</b> <input type="checkbox"/> PCT/NL99/00814 <b>(22) International Filing Date:</b> 29 December 1999 (29.12.99) <b>(30) Priority Data:</b> <u>1010926</u> <u>30 December 1998 (30.12.98)</u> <u>NL</u> <b>(71) Applicant (for all designated States except US):</b> INSTI- TUUT VOOR AGROTECHNOLOGISCH ONDERZOEK (ATO-DLO) [NL/NL]; P.O. Box 17, NL-6700 AA Wageningen (NL). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VAN SOEST, Jeroen, Johannes, Gerardus [NL/NL]; Broekemalaan 2, NL-6703 GL Wageningen (NL). STAPPERS, Frank, H., M. [NL/NL]; Broekeindweg 10, NL-571 NZ Grubbenvorst (NL). VAN SCHIJNDEL, Renée, Josie, Gide [NL/NL]; Schaepmanstraat 117, NL-6702 AS Wageningen (NL). GOTTLIEB, Kornelis, Fester [NL/NL]; Wildervankstraat 12, NL-9643 LC Wildervank (NL). FEIL, Herman [NL/NL]; De Gheijnstraat 10, NL-6717 RG Ede (NL). <b>(74) Agent:</b> DE BRUIJN, Leendert, C.; Nederlandsch Octrooibu- reau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METHOD FOR THE PREPARATION OF STARCH PARTICLES		
<b>(57) Abstract</b> <p>The present invention relates to a method for the preparation of starch particles in a two-phase system, which method comprises at least the following steps: a) a preparation of a first phase comprising a dispersion of starch in water; b) preparation of a dispersion or emulsion of the first phase in a second liquid phase, with the proviso that the second phase is not water; c) cross-linking of the starch present in the first phase; d) separating the starch particles thus formed. According to a first aspect of the invention the second phase consists of a hydrophobic liquid and step b) consists in forming an oil-in-water emulsion, which is then inverted to a water-in-oil emulsion. According to a second aspect of the invention, the second phase consists of a water-miscible non-solvent for starch. Starch particles of very small particles size can be produced in a controlled manner by means of this method.</p>		

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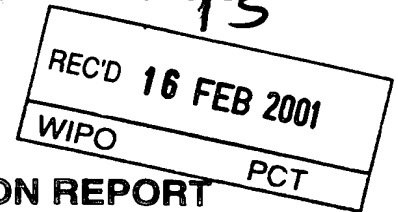
PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

09/8697065





Applicant's or agent's file reference BO 42044	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NL99/00814	International filing date (day/month/year) 29/12/1999	Priority date (day/month/year) 30/12/1998
International Patent Classification (IPC) or national classification and IPC C08B31/00		
Applicant INSTITUUT VOOR AGROTECHNOLOGISCH ONDERZOEK et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.  
  
☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).  
  
 These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☒ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  25/07/2000	Date of completion of this report  13.02.2001
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Kairi, M  Telephone No. +49 89 2399 8672  

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/NL99/00814**

**I. Basis of the report**

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*

**Description, pages:**

1-11 as originally filed

**Claims, No.:**

1-14 as received on 22/01/2001 with letter of 22/01/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL99/00814

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

Novelty (N)	Yes: Claims 1-14
	No: Claims
Inventive step (IS)	Yes: Claims 1-14
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-14
	No: Claims

### 2. Citations and explanations see separate sheet

## VI. Certain documents cited

### 1. Certain published documents (Rule 70.10)

and / or

### 2. Non-written disclosures (Rule 70.9)

see separate sheet

## VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:  
see separate sheet

## VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
see separate sheet

**R It m V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**Article 33(2) PCT**

None of the prior art discloses step b) of Claim 1 or that the second phase is a water-miscible nonsolvent for starch according to Claim 9.

**Article 33(3) PCT**

Closest prior art is considered to be the document DE-A-14 43 359 (D1) which discloses a process to directly obtain crosslinked starch in the form of granulates without requiring pulverization. D1 discloses in Example 1 that 100 g of starch which had been washed with water are dissolved in 280 ccm of water and 240 ccm of an aqueous 5 n solution of sodium hydroxide. The obtained solution is dispersed in a solution of 15 g cellulose acetate butyrate in 500 ccm ethylene dichloride. The dispersion is agitated for one hour in order to stabilize the drops of the starch solution in the dispersing medium. Subsequently 70 g 1,3-dichloropropanol are added. The reaction is performed at 50°C for 10 hours. After work up of the reaction mixture 93 g of a cross-linked product in the form of gel grains are obtained.

The subject-matter of Claim 1 differs from the disclosure in D1 in the step b which discloses i) dispersion or emulsifying of the second hydrophobic phase in the first phase, such that an oil-in-water emulsion is obtained; and ii) inversion of the oil-in-water emulsion to a water-in-oil emulsion.

The subject-matter of Claim 9 differs from D1 in that the second phase is a water-miscible non-solvent for starch.

The object of the present invention is to provide a method for the preparation of starch particles by means of which small starch particles having a particle size of 50 nm to a few mm can be obtained in a simple manner and can be used in pharmacy, cosmetics, foods, paints, coatings, paper, inks and many other applications.

The solution provided is non-obvious, since steps b) i) and ii) of Claim 1 and the feature that the second phase is a water-miscible non-solvent for starch according to Claim 9 are not disclosed in D1 or any other prior art and are not considered to be obvious.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/NL99/00814

**Re Item VI**

**Certain documents cited**

The document WO-A-99 01214 has an International Publication Date of 14.01.1999, an International Filing Date of 01.07.1998 and a Priority Date of 01.07.1997.

The document EP-A-0 900 807 has a Publication Date of 10.03.1999 and a Filing Date of 05.09.1997.

**Re Item VII**

**Certain defects in the international application**

The statement of prior art does not include reference to the closest prior art document DE-A-14 43 359 (D1) (Rule 5.1(a)(ii) PCT).

**Re Item VIII**

**Certain observations on the international application**

There appears to be no support in the description for the subject-matter of Claim 13 (Article 6 PCT).



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/NL99/00814 <b>(22) International Filing Date:</b> 29 December 1999 (29.12.99) <b>(30) Priority Data:</b> 1010926 30 December 1998 (30.12.98) NL <b>(71) Applicant (for all designated States except US):</b> INSTITUUT VOOR AGROTECHNOLOGISCH ONDERZOEK (ATO-DLO) [NL/NL]; P.O. Box 17, NL-6700 AA Wageningen (NL). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VAN SOEST, Jeroen, Johannes, Gerardus [NL/NL]; Broekemalaan 2, NL-6703 GL Wageningen (NL). STAPPERS, Frank, H., M. [NL/NL]; Broekeindweg 10, NL-571 NZ Grubbenvorst (NL). VAN SCHIJNDEL, Renée, Josie, Gide [NL/NL]; Schaepmanstraat 117, NL-6702 AS Wageningen (NL). GOTTLIEB, Kornelis, Fester [NL/NL]; Wildervankstraat 12, NL-9643 LC Wildervank (NL). FEIL, Herman [NL/NL]; De Gheijnstraat 10, NL-6717 RG Ede (NL). <b>(74) Agent:</b> DE BRUIJN, Leendert, C.; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METHOD FOR THE PREPARATION OF STARCH PARTICLES <b>(57) Abstract</b> <p>The present invention relates to a method for the preparation of starch particles in a two-phase system, which method comprises at least the following steps: a) a preparation of a first phase comprising a dispersion of starch in water; b) preparation of a dispersion or emulsion of the first phase in a second liquid phase, with the proviso that the second phase is not water; c) cross-linking of the starch present in the first phase; d) separating the starch particles thus formed. According to a first aspect of the invention the second phase consists of a hydrophobic liquid and step b) consists in forming an oil-in-water emulsion, which is then inverted to a water-in-oil emulsion. According to a second aspect of the invention, the second phase consists of a water-miscible non-solvent for starch. Starch particles of very small particles size can be produced in a controlled manner by means of this method.</p>		

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## Method for the preparation of starch particles

The present invention relates to a method for the preparation of starch particles by means of which small starch particles having a particle size of 50 nm to a few mm can be obtained in a simple manner. In particular small starch particles having a particle size of 50 nm to 100  $\mu$ m, so-called nano- or micro-particles, are highly desirable for a broad range of applications. Small starch particles can be used in pharmacy, cosmetics, foods, paints, coatings, paper, inks and many other applications.

Up to now small particles of this type have been prepared using polymers as starting materials by means of (multiple) emulsion cross-linking or solvent evaporation, spray-drying and other methods (Jiugao, Y. et al., Starch 46 (1994) 252; Arshady, R., Pol. Eng. Sci., 29 (1989), 1747). A number of routes are described in the following patents: PCT/GB/01735, PCT/GB95/00686, PCT/GB92/01692, PCT/GB93/01421, EP 0 213 303 B1. In EP 0 213 303 B1 two immiscible aqueous liquid phases are used as the starting material. In the case of emulsion cross-linking a great deal of mechanical energy is required and it is very difficult to separate off and to purify the particles, which leads to high production costs (for example in PCT/GB93/01692). Evaporation and spray-drying are also expensive techniques which demand the use of large quantities of (usually organic, volatile) solvents. A polymer or starch dissolved in water is always used as the starting material. In PCT/GB95/00686 a combination of a water-soluble and water-insoluble polymer is used as the starting material. However, both are dissolved in two different solvents.

The present invention now provides a method for the preparation of starch particles using a two-phase system with starch as a third main component. The method comprises at least the following steps:

- a) preparation of a first phase comprising a dispersion of starch in water;
- b) preparation of a dispersion or emulsion of the first phase in a second liquid phase, with the proviso that the second phase is not water;
- c) cross-linking of the starch present in the first phase;
- d) separating the starch particles thus formed.

According to the present invention starch is understood to be native starch, granular starch, fractions and derivatives of starch and agricultural raw materials which are rich in starch (containing at least 80 % starch wt./wt.), such as wheat flour. The starch can

originate from a wide variety of natural sources, such as wheat, corn, amylocorn, wax corn, potatoes, quinoa, rice, etc.

Preferably, the starch is granular starch which can be native or modified, for example physically, chemically or enzymatically modified. The starch does not have to be soluble in water cold. Optionally the starch can also be fully or partially gelatinised or melted. A mixture of various types of starch can also be used. For instance, partially soluble, (pre-)gelatinised or modified starch can be added to native starch.

Partially or completely fractionated starch, such as starch enriched in amylose or, on the contrary, enriched in amylopectin, can also be used. Derivatives which can be used are partially or completely hydrolysed starch, such as maltodextrins, in which context hydrolysis can be under the influence of heat or acid, basic or enzymatic hydrolysis, oxidised starch (carboxy, dialdehyde, etc.), carboxylated, chlorinated or sulphated starch, starch that has been rendered hydrophobic (esters, such as acetate, succinate, half-esters, phosphate esters) and phosphated starch, starch ethers (hydroxyalkyl), and the like. Furthermore, starches with combinations of the abovementioned modifications, i.e. bifunctional or multifunctional starch, can also be used. The derivatives can also be granular.

Other carbohydrates or polymers can be used as auxiliaries. These auxiliaries make up at most 15 %, preferably 1 - 10 % (wt./wt. based on starch solids). Said auxiliaries include, in particular, other carbohydrates, such as alginates, pectins and carboxymethylcellulose.

According to a first aspect of the present invention, the second phase is a hydrophobic phase. Said second phase is dispersed or emulsified in the first phase (starch-in-water) in such a way that an oil-in-water (O/W) emulsion is produced (step b i)). Said O/W emulsion is then inverted to a water-in-oil (W/O) emulsion (step b ii)). This process is referred to as "phase inversion" in this application. In the W/O emulsion the aqueous phase consists of the first water-in-starch phase. The starch can be granular, partially gelatinised or dissolved here. Following the phase inversion step, the starch particles are cross-linked and then separated.

The cross-linking reaction can already have been started before or during phase inversion. This method can be used in particular if the conditions for the cross-linking reaction are such that the cross-linking reaction proceeds slowly. Complete cross-linking in general takes place after phase inversion.

The starch does not yet have to be completely gelatinised at the start of the method. According to a preferred embodiment of the invention, partial or complete further gelatinising of the granular starch is effected during, before or after phase inversion. The starch can remain partially granular during cross-linking. Gelatinising can be effected by means of raising the temperature or by adding salts, such as hydroxides, or by a combination thereof.

It is advantageous if in step b) the ratio of hydrophobic phase:water in the O/W emulsion is of the order of magnitude of 80:20 to 20:80. Preferably, the ratio of hydrophobic phase:water in the O/W emulsion is between 60:40 and 40:60 (V/V).

All liquids which are not miscible with water are suitable as hydrophobic phase. Examples of these are hydrocarbons (alkanes, cycloalkanes), ethers, esters, halogeno-hydrocarbons, di- and triglycerides, fats, waxes and oils. Examples of oils or fats are palm oil, kernel oil, sunflower oil and salad oil. A number of apolar liquids are octane, dodecane, toluene, decalin, xylene, higher alcohols such as pentanol and octanol, or a mixture thereof. Paraffin oil, hexane or cyclohexane are preferably used. Preferably the viscosity of the hydrophobic phase is close to the viscosity of the starch/water phase. The miscibility of the water/starch phase with the hydrophobic phase preferably has to be as low as possible.

Preferably the O/W emulsion is stabilised with the aid of a surfactant. Phase inversion, i.e. the inversion from O/W emulsion to a W/O emulsion (step b) ii)), can take place in various ways. 1) If a surfactant is used which is temperature-sensitive, the phase inversion can be induced by raising the temperature. 2) The O/W emulsion can be destabilised by adding another surfactant. This surfactant stabilises a W/O emulsion. 3) Phase inversion can be obtained by adding a hydrophobic liquid. 4) Phase inversion can also be obtained with the aid of the addition of salts.

Phase inversion by means of raising the temperature may be mentioned first. Raising the temperature gives rise to a shift of the surfactant molecules at the O/W interface towards the oil phase. The result of this is that the protection which the polar head provides against coalescence of the hydrophobic phase also decreases. At a certain temperature, which is dependent on, for example, the hydrophobic phase, type of surfactant and type and concentration of starch in the aqueous phase, the protection has decreased to such an extent that all oil droplets coalesce and the emulsion changes over or inverts from O/W to W/O.



The phase inversion temperature (PIT) is dependent on the chosen (water/starch)/oil (hydrophobic phase)/surfactant system. The surfactant concerned must preferably have an equal affinity for water and the hydrophobic phase, for example an oil. This is expressed in the HLB (hydrophilic-lipophilic balance) value. Preferably surfactants are used which have a HLB value of 8 to 20 or more preferentially of 10 to 15. The higher the HLB value the greater is the affinity of the surfactant for the aqueous phase. If this value becomes too high a much greater rise in temperature (or the addition of surfactant or hydrophobic liquid or salt) is needed in order to make phase inversion possible, or there is even no longer any phase inversion at all.

In principle, a wide variety of surfactants or emulsifiers can be used, such as fatty acid monoglycerides, such as Dimodan, Acidan (distilled monoglyceride) and glycerol monostearate, citric, lactic and acetic acid esters of fatty acids (Cetodan, Lactodan, Panodan, Promodan), propylene glycol esters of fatty acids (Triodan), sorbitan monolaurate, sorbitan monopalmitate, calcium stearate, ethoxylated and succinylated monoglycerides, glucose and sucrose esters; also fatty acid alcohols (cetanol, palmitol, stearyl alcohol), free fatty acids, lipids, phospholipids, lecithins, glycolipids and glycols. Examples of very suitable surfactants are those having a polar polyoxyethylene head. Such surfactants are, in particular, marketed under the trade name Tween. Tween-85 (polyoxyethylene (20) sorbitan trioleate,  $HLB = 11 \pm 1$ ) is preferably used.

As stated above: the temperature at which phase inversion takes place is dependent on various factors, such as the type and to a lesser extent the concentration of the surfactant. The PIT can, for example, be lowered by :

- \* increasing the salt concentration in the emulsion;
- \* reducing the water:oil ratio;
- \* adding an alcohol;
- \* raising or lowering the pH, depending on the type of surfactant.

Preferably the water/oil (hydrophobic phase)/surfactant system is so chosen that a temperature rise of only 20 °C, preferably only 10 °C, is sufficient to effect phase inversion. Preferably phase inversion takes place at between 0 and 80 °C, more preferably at somewhat above room temperature (approx. 25 - 40 °C).

A second method for allowing phase inversion to take place is the addition of a second surfactant. Said second surfactant differs from the surfactant used to stabilise the O/W emulsion. If the O/W emulsion has been stabilised with Tween 80, Span 80 can be

added, for example.

Furthermore, the changeover from O/W emulsion to W/O emulsion is obtained by adding a hydrophobic liquid or a salt to the O/W emulsion. The change or inversion takes place by changing the volume fractions of the water and oil phases or, respectively, changing the surface tension at the interface. In fact, the addition of a hydrophobic liquid or salt to the O/W emulsion can also be regarded as lowering the phase inversion temperature.

One advantage of the use of this method (phase inversion) is that the formation of the W/O emulsion is a spontaneous process, so that little mechanical energy is needed for emulsifying the system. This also offers advantages when the system is scaled up. Especially when the PIT method is used, separating off the particles is simple in many cases. This can be effected by means of lowering the temperature, as a result of which the W/O emulsion is destabilised. Separation can also be achieved by adding apolar solvents, preferably an apolar alcohol, more preferably cyclohexanol or cyclooctanol.

Another advantage of this system is that the particle size can be adjusted to that desired by adjusting the process conditions, such as by suitable choice of the components of the system.

Following phase inversion the starch that has been dispersed or, optionally partially, dissolved in the aqueous phase is cross-linked. The cross-linking reaction can be started before, during or after phase inversion. As a result of this reaction discrete starch particles are produced. These particles can then be separated off.

Cross-linking can be effected by means of a cross-linking agent which preferably is added to the starch/water phase. This can take place before phase inversion or during or just after phase inversion, which mainly is determined by the rate of reaction. Depending on the cross-linking agent, cross-linking can be initiated by adding a catalyst, such as a base, acid or salt.

Cross-linking preferably takes place at between 0 and 80 °C, preferably between 10 and 60 °C. It is obvious that cross-linking takes place at a temperature which is above the phase inversion temperature, preferably at least 10 °C and more preferentially at least 20 °C above the phase inversion temperature.

Preferably 5 to 1000 mmol, more preferably 20 - 500 mmol, cross-linking agent is used per mol anhydroglucose unit.

Cross-linking agents which can be used are the most common bifunctional or

multifunctional reagents. Examples of cross-linking agents are the common cross-linking agents such as epichlorohydrin, glyoxal, trisodium trimetaphosphate, phosphoryl chloride or an anhydride of a dibasic or polybasic carboxylic acid. However, the use of a phosphate, such as trisodium trimetaphosphate, as cross-linking agent is particularly preferred. In these cases the catalyst can be a base such as sodium hydroxide.

A variety of other cross-linking agents are possible when modified starches are used. In the case of dialdehyde-starch the cross-linking agent can be, for example, a diamine or diamide, such as urea, tetramethylenediamine or hexamethylenediamine, in which case an acid can be used as catalyst.

Cross-linking can also be carried out using a diamine or a diol in the case of, for example, carboxymethylstarch or dicarboxystarch. However, here cross-linking can also, and advantageously, be achieved by internal ester formation, which can be catalysed by a multivalent metal ion such as calcium, magnesium, aluminium, zinc or iron, preferably calcium. Another possible starting material is cationic or aminoalkyl starch, which can be cross-linked in situ using a dicarboxylic acid or a dialdehyde.

A few other cross-linking agents are: functional epoxides such as diepoxybutane, diglycidyl ether and alkylene bis-glycidyl ethers, dichlorohydrin, dibromohydrin, adipic anhydride, glutaraldehyde, amino acids and borax.

In a number of cases it is also possible to allow a chemical modification of the starch, for example a carboxymethylation or cationisation reaction, to take place simultaneously during the cross-linking reaction.

According to a second aspect of the present invention the second phase consists of a non-solvent for starch that is readily (or completely) miscible with water over a broad concentration range. At a certain ratio between the non-solvent and water the system is no longer completely miscible and phase separation occurs, small droplets of a starch aqueous phase being present in a continuous non-solvent phase.

According to this embodiment the present invention comprises a method for the preparation of starch particles in a two-phase system, wherein the second phase is a water-miscible non-solvent for starch, which method comprises:

- a) preparation of a first phase comprising a dispersion of starch in water;
- b) addition of the second phase to the first phase such that phase separation occurs;
- c) cross-linking of the starch present in the first phase; and
- d) separating the starch particles thus formed.

Any liquid which is miscible with water and in which starch does not dissolve can be used as non-solvent for starch. Examples of such non-solvents are acetone, methanol, ethanol and isopropanol.

Ethanol is preferably used. The quantity of ethanol, during reaction, is preferably  
5 between 20 and 75 %, more preferably between 45 and 55 %, with respect to the quantity of the first starch-in-water phase. The condition is that a phase-separated system is obtained. The quantity is dependent on the other components, such as the starch.

Preferably, the preparation is carried out at 0 - 80 °C, more preferably 10 - 60 °C.

The method of cross-linking with this method corresponds to that which has been  
10 described above. Preferably 5 to 1000 mmol, more preferably 20 - 500 mmol, cross-linking agent is used per mol anhydroglucose unit.

With this method as well the starch does not yet have to be completely gelatinised at the start of the method. According to a preferred embodiment of the invention, partial or complete further gelatinising of the granular starch is effected during, before or after the  
15 addition of the non-solvent to the first phase. The starch can remain partially granular during cross-linking.

The particle size of these particles is between 50 nm and 100 µm. The particle size is dependent on, inter alia, starch and cross-linking agent type and concentration, reaction time and the type of non-solvent. This method as well offers the advantage that the particle  
20 size can be adjusted by adjusting the process conditions, including the various components.

Following cross-linking the particles can be separated off in a very simple manner by means of centrifuging or filtering off and drying. If necessary a little additional non-solvent is added to destabilise the system. The particles can be used immediately in applications in suspension, after partial drying. The particles can be dried in air, optionally  
25 after washing with water, ethanol or acetone, etc., or using existing drying techniques, such as roller drying, freeze drying or spray drying.

Another advantage of this method for the preparation of particles is that no surfactants are required and no acid or salt is needed to be able to separate off the particles. Consequently, re-use of the non-solvent is also possible in a simple manner.

30 The starch particles can be used, inter alia, in paper, textiles, explosives, foams, adhesives, hot melts, detergents, hydrogels, fertilisers, foods, artificial odours and flavourings, pharmaceutical and cosmetic products, tissues, soil improvers, pesticides, coatings, coatings removable by a mild treatment, for instance by means of enzymes or hot

water, paints, inks, toners, organic reactions, catalysis, ceramics and diagnostic agents. The quantities to be used are the quantities customary for the use concerned.

### Example 1

13 g Paselli SA2 (Avebe) was dispersed in 80 g water containing 10 g NaCl. The dispersion was added to 110 g paraffin oil containing 7 g Tween 85. The O/W emulsion was brought to 22 °C. 0.21 g NaOH and 1.2 ml epichlorohydrin (ECH) in 2 ml water was then added and the whole was heated to 50 °C. The phase inversion temperature PIT2 (after the addition of alkali and thus during cross-linking) of the emulsion was 25 °C. The reaction time was a few hours.

To initiate separation, 0.52 ml 37 % HCl and 50 ml water were added. The temperature was brought to 21 °C. This is the phase inversion temperature after neutralisation of the emulsion (PIT3). The phase inversion temperature before the addition of acid, PIT2, is usually somewhat higher than PIT3. It was possible to centrifuge or filter off the particles easily and rapidly. An estimate of the particle size (<600 nm) was made with the aid of light microscopy. The particles are spherical.

### Example 2

60 g Paselli SA2 (Avebe) was dispersed in 400 g water containing 45 g NaCl. The dispersion was added to 500 g paraffin oil containing 35 g Tween 85. The O/W emulsion was brought to 20 °C. 0.21 g NaOH and 1.2 ml epichlorohydrin (ECH) in 2 ml water were added and the whole was heated to 50 °C. The PIT2 of the W/O emulsion was 25 °C. The reaction time was 16 h.

To initiate separation, 5 g 37 % HCl in 200 ml water was added. The temperature was brought to 20 °C. It was possible to centrifuge or filter off the particles easily and rapidly. An estimate of the particle size (<600 nm) was made with the aid of light microscopy. The particles are spherical.

### Example 3

60 g Paselli SA2 (Avebe) was dispersed in 400 g water containing 10 g NaCl. The dispersion was added to 500 g paraffin oil containing 35 g Tween 85. The O/W emulsion was brought to 20 °C. The phase inversion temperature PIT1 before cross-linking of this emulsion is 25 °C. 0.95 g NaOH and 3 ml water and 30 g trisodium trimetaphosphate

(TSTP) were added and the whole was heated to 55 °C. Phase inversion took place at 25 °C. The reaction time was 3.5 h.

To initiate separation, 2.4 g 37 % HCl in 200 ml water was added. The temperature was reduced to below 25 °C (*i.e.* PIT3). The particles were separated off by means of alternately heating and cooling about a temperature of 20 °C (phase inversion temperature after neutralisation, *i.e.* PIT3). An estimate of the particle size (<600 nm) was made with the aid of light microscopy.

#### Example 4

200 g Paselli SA2 (Avebe) was dispersed in 1 l water containing 70 g TSTP. The dispersion was added to 1000 ml paraffin oil containing 40 g Tween 85. The O/W emulsion was brought to 20 °C. Phase inversion took place at 25 °C (PIT2; PIT1 is 24 °C). 2.5 g NaOH in 10 ml water was added and the whole was heated to 50 °C. The reaction time was 16 h.

To initiate separation, 6.25 g 37 % HCl in 500 ml water was added. The temperature was reduced to below 22 °C (PIT3). The particles were separated off by means of alternately heating and cooling about a temperature of 22 °C (phase inversion temperature after neutralisation, *i.e.* PIT3). An estimate of the particle size (<600 nm) was made with the aid of light microscopy. The particles are spherical.

#### Example 5

6 g Paselli SA2 was dispersed in 40 g water containing 3 g NaCl. The dispersion was added to 55 g paraffin oil containing 3.5 g Tween 85. The O/W emulsion was brought to 20 °C. 0.314 g NaOH in 2 ml water was added. 0.3 g GMAC (cationic reagent) in 2 ml water was then added with 1 ml ECH. The whole was heated to 50 °C. The reaction time was 6 h.

To initiate separation, 0.79 g 37 % HCl in 20 ml water was added. The temperature was reduced to below 30 °C. The PIT3 was 30 °C. An estimate of the particle size was made with the aid of light microscopy. It was possible to lower the PIT3 by adding NaCl.

#### Example 6

12 g native potato starch (PN) was dispersed in demineralised water (600 ml) in a glass beaker with a top stirrer. Sodium hydroxide (2 g in 25 ml demineralised water) was

added to the starch dispersion until a homogeneous, thick, gelatinous mass was obtained without lumps. Ethanol (EtOH, 450 ml) was then introduced slowly into the starch/water phase until a (milky, white) two-phase system was formed. After a stable situation had been obtained, 4 g TSTP was added. The reaction was carried out at room temperature for 24 h. Following reaction, ethanol (250 ml) was added until a sediment of water containing the starch particles and an EtOH-water upper layer had formed. The EtOH-water layer was poured off. Optionally it is possible to centrifuge first (3 min at 3000 rpm). If necessary the starch layer is also washed a number of times with water until virtually all EtOH has disappeared. Light microscopy showed that the starch was partially gelatinised and contained residual granules.

### Example 7

500 g native potato starch (PN) was dispersed in demineralised water (25 l) in a glass beaker with top stirrer. Sodium hydroxide (333 g) was added to the starch dispersion until a homogeneous, thick, gelatinous mass was obtained without lumps. Ethanol (EtOH, 10.4 l) was then added slowly to the starch/water phase until a (milky, white) two-phase system was formed. After a stable situation had been obtained, 366.7 g TSTP was added. The reaction was carried out at room temperature for 24 h. The EtOH-water layer was poured off as far as possible after the particles had formed a sediment. The water/starch layer was spray-dried using a Niro Mobile Minor spray dryer (position 2 at 150 °C). The particle size determined by electron microscopy was approximately 1 - 10 µm.

### Example 8

18 g native wax corn starch (WCN) was dispersed in demineralised water (600 ml) in a glass beaker with top stirrer. Sodium hydroxide (6 g in 25 ml demineralised water) was added to the starch dispersion until a homogeneous, thick, gelatinous mass was obtained without lumps. Ethanol (EtOH, 250 ml) was then added slowly to the starch/water phase until a (milky, white) two-phase system was formed. After a stable situation had been obtained, 4 g TSTP was added. The reaction was carried out at room temperature for 24 h. Following reaction, ethanol (156 ml) was added until a sediment of water containing the starch particles and an EtOH-water top layer had formed. An ultrasonic bath was used during the addition. The EtOH-water layer was poured off. Centrifuging (3 min at 3000 rpm) can be carried out if appropriate. If necessary, the starch

layer is also washed a number of times with water until virtually all EtOH has disappeared.

#### Example 9

Particles were made from Floc-gel and Paselli SA2 starch (Avebe) in a manner identical to that in Examples 6, 7 and 8. However, the quantities of EtOH added for separation (second quantity) were 230 and 255 ml, respectively.

#### Example 10

100 g cationic starch (Avebe, DS = 0.044) was dispersed in approximately 300 ml water. 20 g ECH and 150 mg H<sub>2</sub>SO<sub>4</sub> were added to this dispersion. The starch suspension was then kept at 70 °C for 4 hours in order to achieve acid coupling of the ECH to the starch. The starch was gelatinised at the same time. The starch solution was then cooled to room temperature.

Approximately 300 ml ethanol was then added; phase separation occurred at this water/ethanol ratio, which could be seen by the fact that the solution became turbid and could also be seen by light microscopy. As soon as phase separation occurred the pH was raised by slowly adding a solution of 1 g NaOH in 50 ml of a 1:1 water/ethanol mixture. The cross-linking reaction was started by this means. After 18 hours additional ethanol was added, after which the cross-linked starch particles were removed from the ethanol by centrifuging. The particles were washed and thickened to give a suspension containing approximately 30 % solids.



**Claims**

1. Method for the preparation of starch particles in a two-phase system, which method comprises at least the following steps:

- a) preparation of a first phase comprising a dispersion of starch in water;
- b) preparation of a dispersion or emulsion of the first phase in a second liquid phase, with the proviso that the second phase is not water;
- c) cross-linking of the starch present in the first phase;
- d) separating the starch particles thus formed.

2. Method according to Claim 1, wherein the second phase is a hydrophobic phase, which method comprises the following steps:

- a) preparation of a first phase comprising a dispersion of starch in water;
- b i) dispersion or emulsifying of the second phase in the first phase, such that an oil-in-water emulsion is obtained;
- ii) inversion of the oil-in-water emulsion to a water-in-oil emulsion;
- c) cross-linking of the starch present in the first phase;
- d) separating the starch particles thus formed.

3. Method according to Claim 2, wherein the starch is completely or partially gelatinised before, during or after step b) ii).

4. Method according to Claim 2, wherein in step b) i) the hydrophobic phase:water ratio is 80:20 to 20:80, preferably 60:40 to 40:60.

5. Method according to Claim 2, 3 or 4 wherein the oil-in-water emulsion contains a surfactant.

6. Method according to Claim 5, wherein the surfactant has an HLB value of 8 to 20, preferably of 10 to 15.

7. Method according to Claim 5 or 6, wherein step b) ii) comprises raising the temperature of the oil-in-water emulsion until inversion takes place.

8. Method according to Claim 5 or 6, wherein step b) ii) comprises the addition of a second surfactant to the oil-in-water emulsion, such that inversion to a water-in-oil emulsion takes place.

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9. Method according to Claim 5 or 6, wherein step b) ii) comprises the addition of a hydrophobic liquid to the oil-in-water emulsion such that inversion to a water-in-oil emulsion takes place.

10 10. Method according to Claim 1, wherein the second phase is a water-miscible non-solvent for starch, which method comprises:

- a) preparation of a first phase comprising a dispersion of starch in water;
- b) addition of the second phase to the first phase such that phase separation occurs;
- c) cross-linking of the starch present in the first phase; and
- 15 d) separating the starch particles thus formed.

11. Method according to Claim 10, wherein the water-miscible non-solvent for starch is ethanol or acetone, preferably ethanol.

20 12. Method according to Claim 10 or 11, wherein the starch is completely or partially gelatinised before, during or after step b) or c).

13. Method according to one of the preceding claims, wherein the starch consists of partially modified starch.

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14. Method according to one of the preceding claims, wherein the starch content in the first phase is 1 - 50 % (m/m), preferably 5 to 25 % (m/m).

15. Method according to one of the preceding claims, wherein cross-linking is carried  
30 out with the aid of a cross-linking agent, which is preferably trisodium trimetaphosphate or epichlorohydrin.

Claims

1. Method for the preparation of starch particles in a two-phase system, which method comprises at least the following steps:

- a) preparation of a first phase comprising a dispersion of starch in water;
- b) preparation of a dispersion or emulsion of the first phase in a second liquid phase, with the proviso that the second phase is not water;
- c) cross-linking of the starch present in the first phase;
- d) separating the starch particles thus formed.

2. Method according to Claim 1, wherein the second phase is a hydrophobic phase, which method comprises the following steps:

- a) preparation of a first phase comprising a dispersion of starch in water;
- b)
  - i) dispersion or emulsifying of the second phase in the first phase, such that an oil-in-water emulsion is obtained;
  - ii) inversion of the oil-in-water emulsion to a water-in-oil emulsion;
- c) cross-linking of the starch present in the first phase;
- d) separating the starch particles thus formed.

3. Method according to Claim 2, wherein the starch is completely or partially gelatinised before, during or after step b) ii).

4. Method according to Claim 2, wherein in step b) i) the hydrophobic phase:water ratio is 80:20 to 20:80, preferably 60:40 to 40:60.

5. Method according to Claim 2, 3 or 4 wherein the oil-in-water emulsion contains a surfactant.

6. Method according to Claim 5, wherein the surfactant has an HLB value of 8 to 20, preferably of 10 to 15.

7. Method according to Claim 5 or 6, wherein step b) ii) comprises raising the temperature of the oil-in-water emulsion until inversion takes place.

8. Method according to Claim 5 or 6, wherein step b) ii) comprises the addition of a second surfactant to the oil-in-water emulsion, such that inversion to a water-in-oil emulsion takes place.

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9. Method according to Claim 5 or 6, wherein step b) ii) comprises the addition of a hydrophobic liquid to the oil-in-water emulsion such that inversion to a water-in-oil emulsion takes place.

10. Method according to Claim 1, wherein the second phase is a water-miscible non-solvent for starch, which method comprises:

- a) preparation of a first phase comprising a dispersion of starch in water;
- b) addition of the second phase to the first phase such that phase separation occurs;
- c) cross-linking of the starch present in the first phase; and
- 15 d) separating the starch particles thus formed.

11. Method according to Claim 10, wherein the water-miscible non-solvent for starch is ethanol or acetone, preferably ethanol.

20 12. Method according to Claim 10 or 11, wherein the starch is completely or partially gelatinised before, during or after step b) or c).

13. Method according to one of the preceding claims, wherein the starch consists of partially modified starch.

25

14. Method according to one of the preceding claims, wherein the starch content in the first phase is 1 - 50 % (m/m), preferably 5 to 25 % (m/m).

15. Method according to one of the preceding claims, wherein cross-linking is carried  
30 out with the aid of a cross-linking agent, which is preferably trisodium trimetaphosphate or epichlorohydrin.

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## New Claims

(41)

1. Method for the preparation of starch particles in a two-phase system, which method comprises the following steps:
  - a) preparation of a first phase comprising a dispersion of starch in water;
  - b)
    - i) dispersion or emulsifying of a second phase, which is a hydrophobic phase in the first phase, such that an oil-in-water emulsion is obtained;
    - ii) inversion of the oil-in-water emulsion to a water-in-oil emulsion;
  - c) cross-linking of the starch present in the first phase;
  - d) separating the starch particles thus formed.
2. Method according to Claim 2, wherein the starch is completely or partially gelatinised before, during or after step b) ii).
3. Method according to Claim 1, wherein in step b) i) the hydrophobic phase:water ratio is 80:20 to 20:80, preferably 60:40 to 40:60.
4. Method according to Claim 1, 2 or 3 wherein the oil-in-water emulsion contains a surfactant.
5. Method according to Claim 4, wherein the surfactant has an HLB value of 8 to 20, preferably of 10 to 15.
6. Method according to Claim 4 or 5, wherein step b) ii) comprises raising the temperature of the oil-in-water emulsion until inversion takes place.
7. Method according to Claim 4 or 5, wherein step b) ii) comprises the addition of a second surfactant to the oil-in-water emulsion, such that inversion to a water-in-oil emulsion takes place.
8. Method according to Claim 4 or 5, wherein step b) ii) comprises the addition of a hydrophobic liquid to the oil-in-water emulsion such that inversion to a water-in-oil emulsion takes place.

9. Method for the preparation of starch particles in a two-phase system, which method comprises:

- a) preparation of a first phase comprising a dispersion of starch in water;
- b) addition of a second phase, which is a water-miscible non-solvent for starch to the first phase such that phase separation occurs;
- c) cross-linking of the starch present in the first phase; and
- d) separating the starch particles thus formed.

10. Method according to Claim 9, wherein the water-miscible non-solvent for starch is ethanol or acetone, preferably ethanol.

11. Method according to Claim 9 or 10, wherein the starch is completely or partially gelatinised before, during or after step b) or c).

12. Method according to one of the preceding claims, wherein the starch consists of partially modified starch.

13. Method according to one of the preceding claims, wherein the starch content in the first phase is 1 - 50 % (m/m), preferably 5 to 25 % (m/m).

14. Method according to one of the preceding claims, wherein cross-linking is carried out with the aid of a cross-linking agent, which is preferably trisodium trimetaphosphate or epichlorohydrin.

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